Nucleation Energy Barriers and the Coarsening of Faceted Crystals

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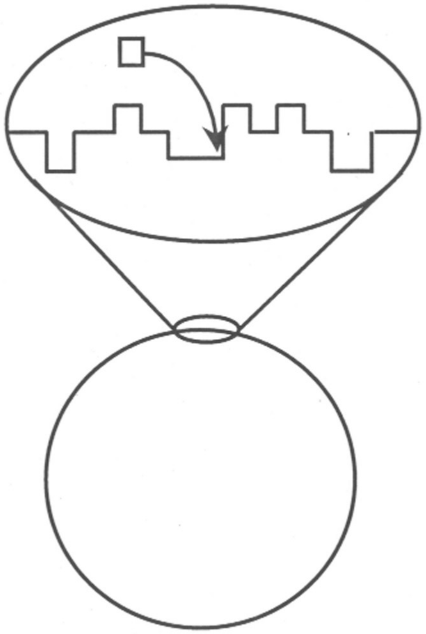
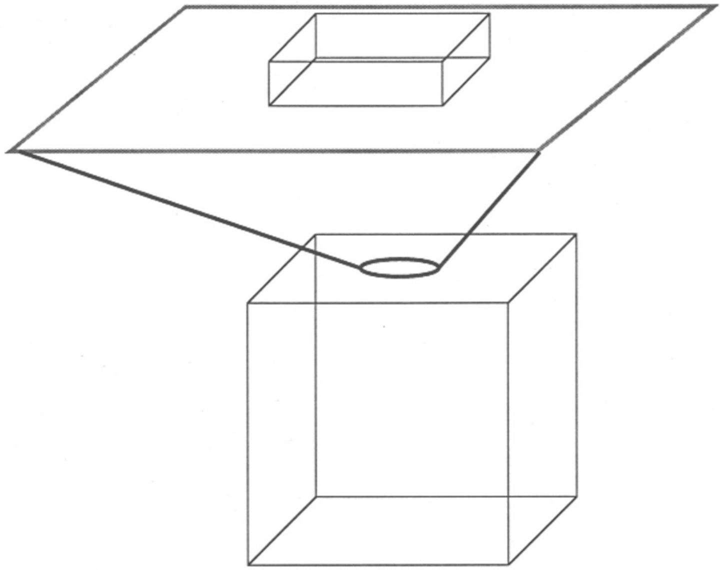
Growth Resistance



On a "rough surface," there is no barrier to the attachment of atoms (assumption in LSW theory).

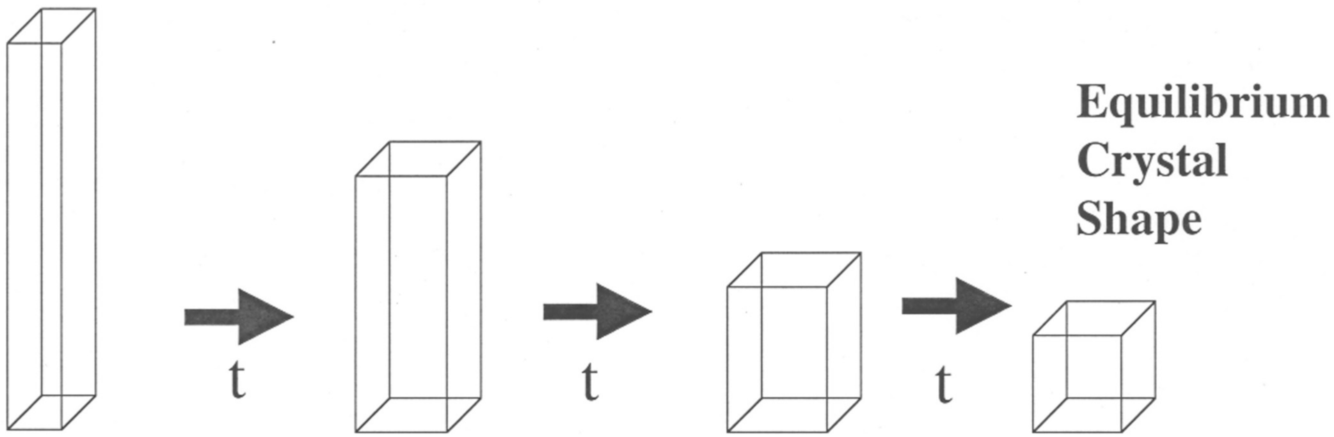


On a facet, there is a nucleation barrier. The creation of new edges must be balanced by the volume energy gained by reducing the chemical potential of the material that condenses.

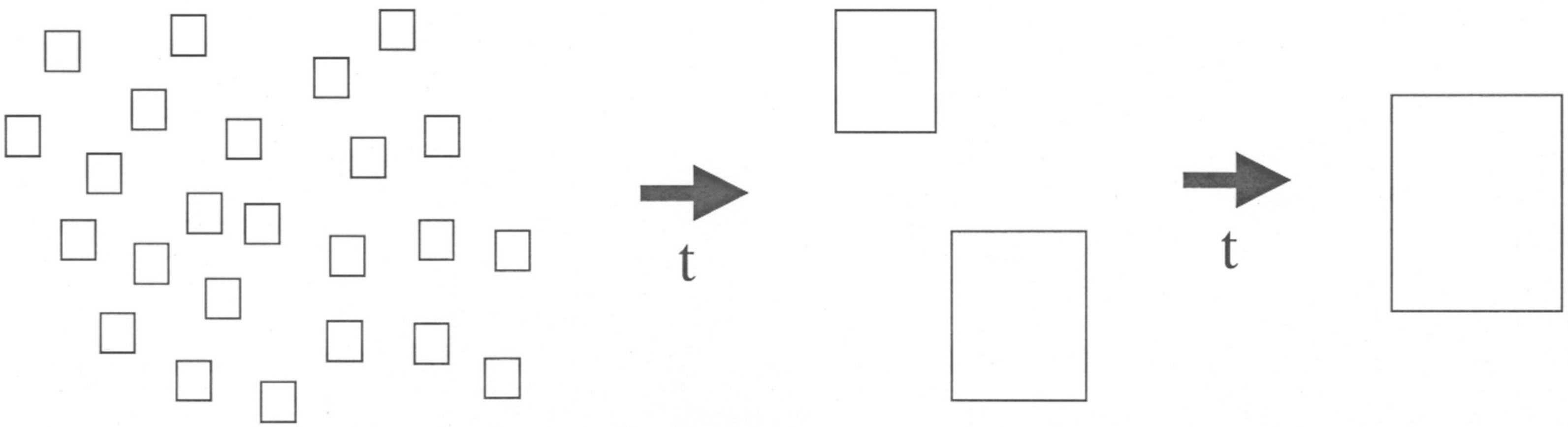
Burton, Cabrera, Frank, Philos. Trans. R. Soc. London, Ser. A, 243 300-58 (1951).

Situations with Low Supersaturation

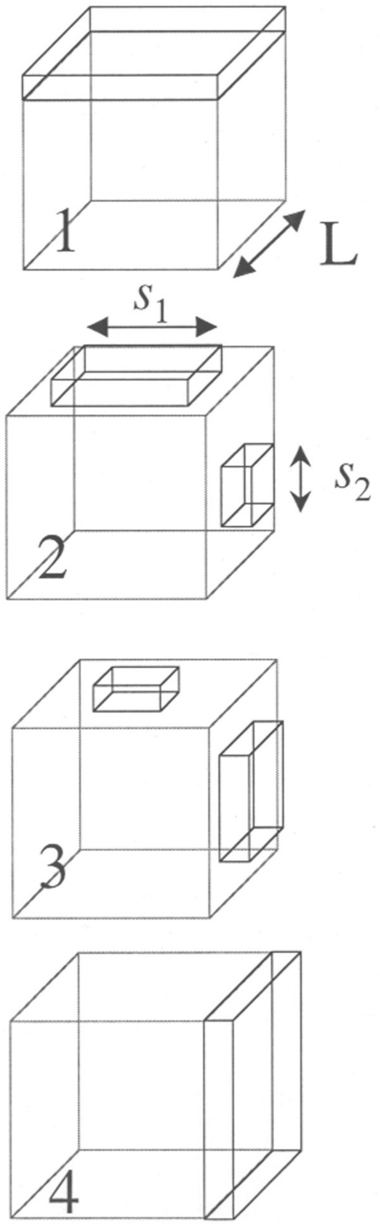
1. Morphological Evolution



2. Coarsening

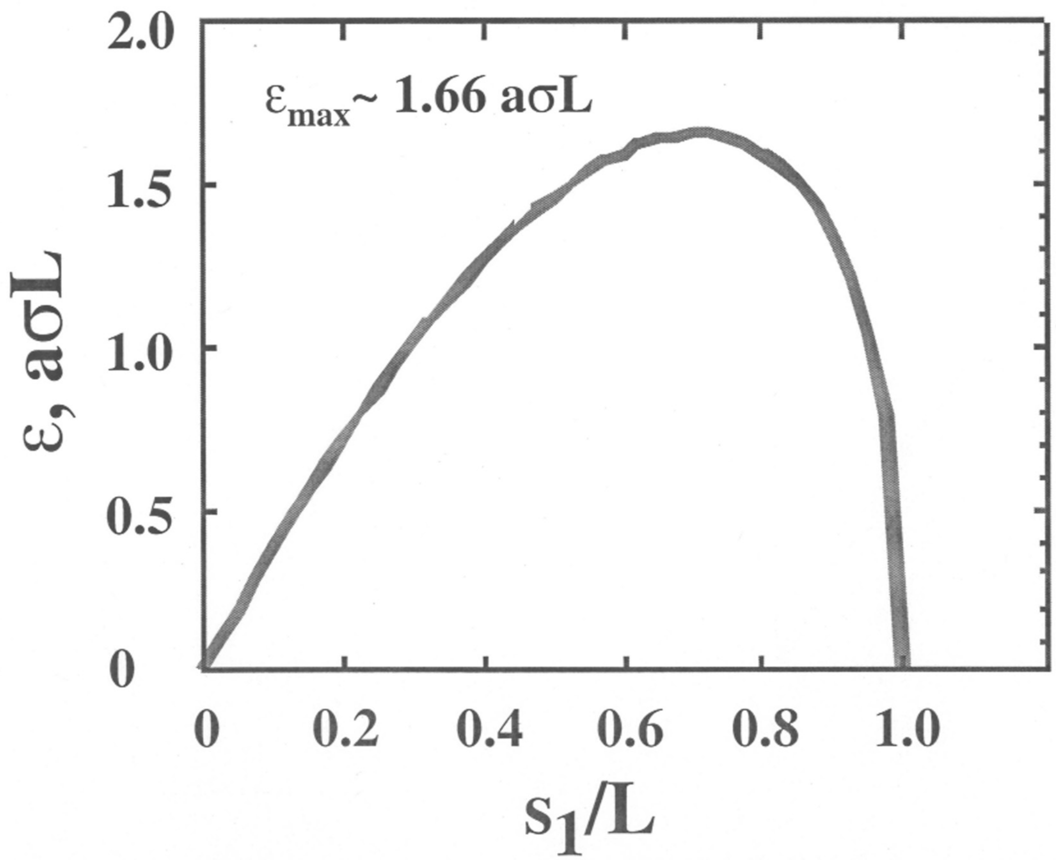


The Barrier to Shape Changes: Cube



$$\varepsilon(s_1) = 4a\sigma s_1 + 4a\sigma s_2 - 4a\sigma L$$

$$\varepsilon(s_1) = 4a\sigma s_1 + 4a\sigma (L^2 - s_1{}^2)^{1/2} - 4a\sigma L$$

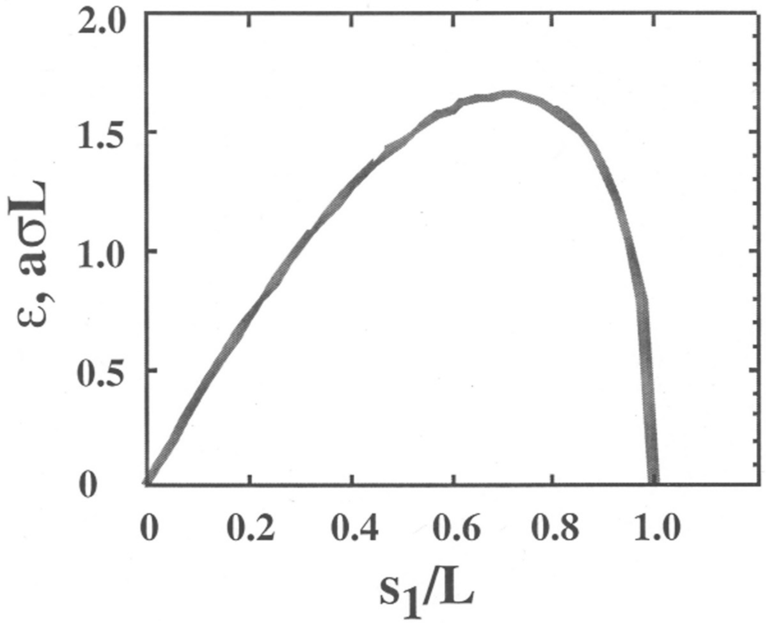


Size of the Nucleation Energy Barrier

$\varepsilon_{max} \sim 1.66\, a\sigma L$

Let S = 1 μm
a = 2.5 Å
$\sigma = 1\ J/m^2$
$kT = 10^{-20}\ J$

$\varepsilon_{max} = 1.66 a\sigma S = 4 \times 10^4\ kT$



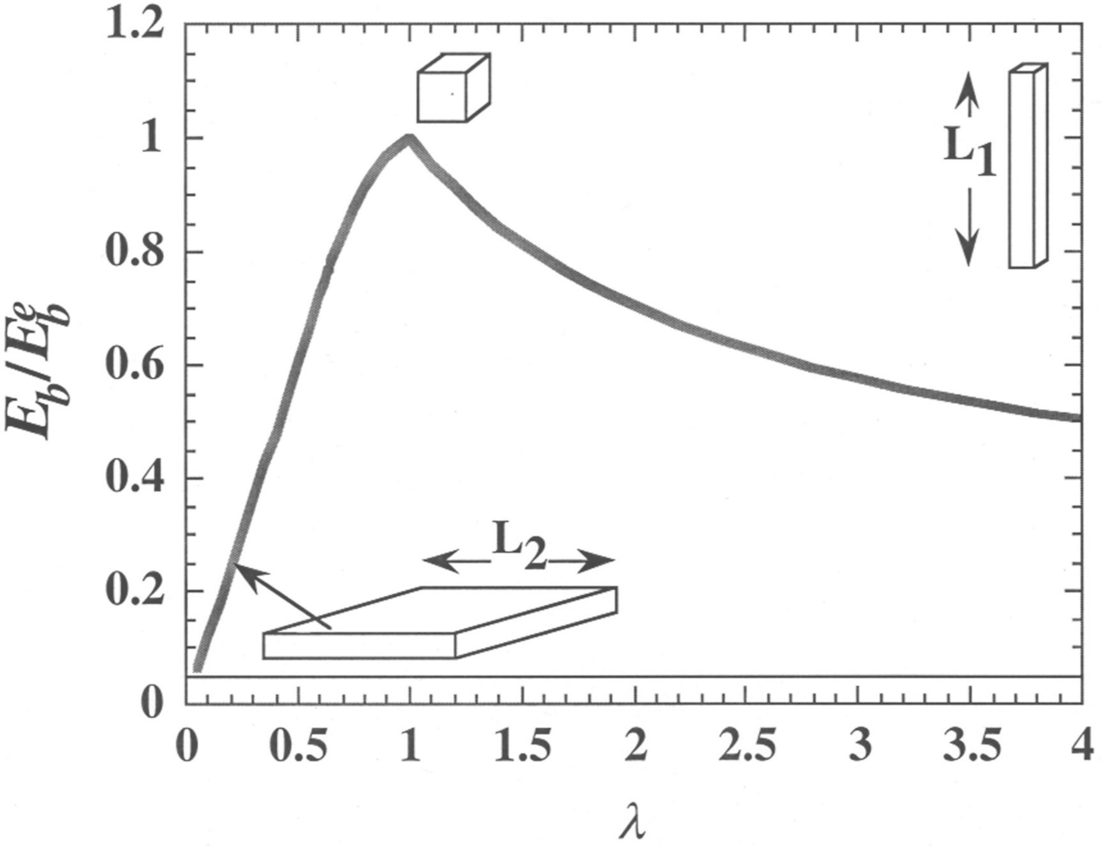
• **Barriers larger than 60kT are never surmounted**

Let S = 1 nm
a = 2.5 Å
$\sigma = 1\ J/m^2$
$kT = 10^{-20}\ J$

$\varepsilon_{max} = 1.66 a\sigma S = 40\ kT$

• Only "nanocrystals" are able to provide equivalent supersaturations necessary for island nucleation.

Nonequilibrium Shapes: Cube



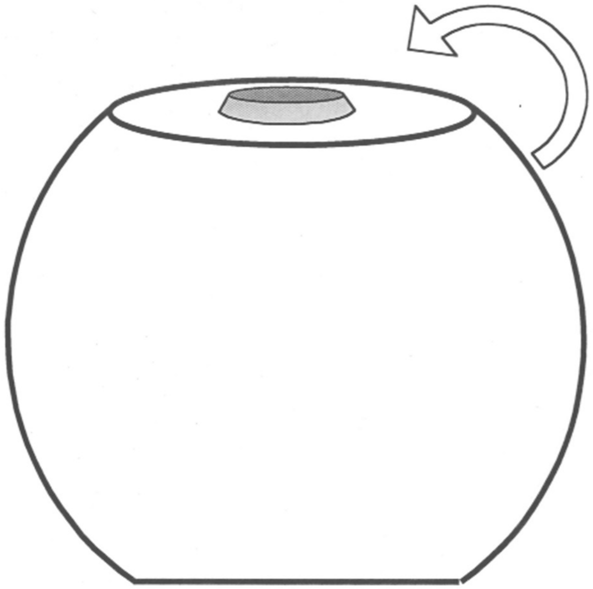
Volume Conservation

$L_1(L_2)^2 = L^3$

$\lambda = (L_1/L)$

The nucleation energy barrier remains significant even for large departures from the equilibrium crystal shape.

The Barrier on Shapes with Rough Surfaces

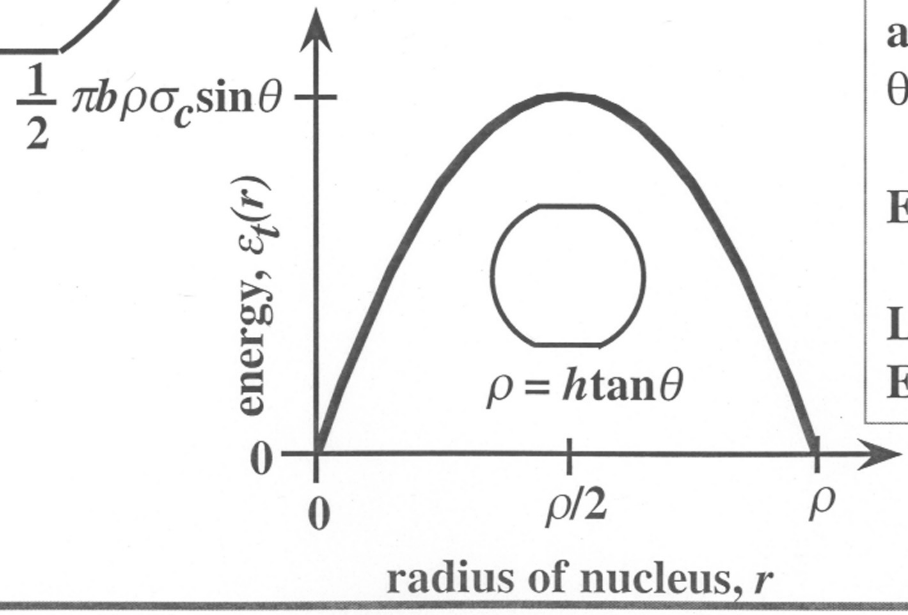


$$\sigma_s = \sigma_c \cos\theta$$

$$\varepsilon_t(r) = 2\pi a r \sigma_c \sin\theta - \pi a r^2 \left(\frac{2\sigma_c}{R} \right)$$

$$= 2\pi a \sigma_c \sin\theta \left(r - \frac{r^2}{\rho} \right)$$

(for $0 \le r \le \rho$)



Let R = 1 μm,
a = 2.5 Å, σ = 1 J/m^2,
θ = 10° , kT = 10^{-20} J

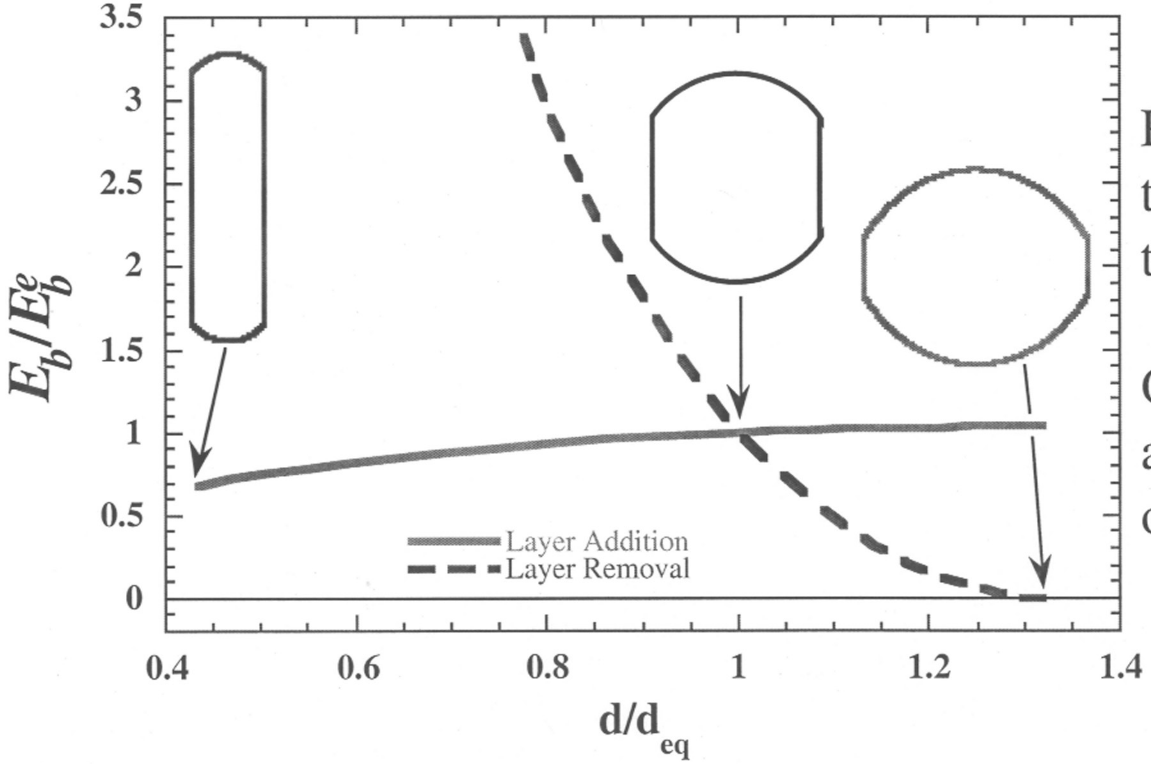
E$_b$ = 1 x 10^3 kT

Let R = 10 nm
E$_b$ = 10 kT

Nonequilibrium Truncated Sphere

$$E_b(+)/E_b^e = 2/R\kappa$$

$$E_b(-)/E_b^e = (2/R\kappa)[R\kappa(\rho/\rho_e)-1]^2$$



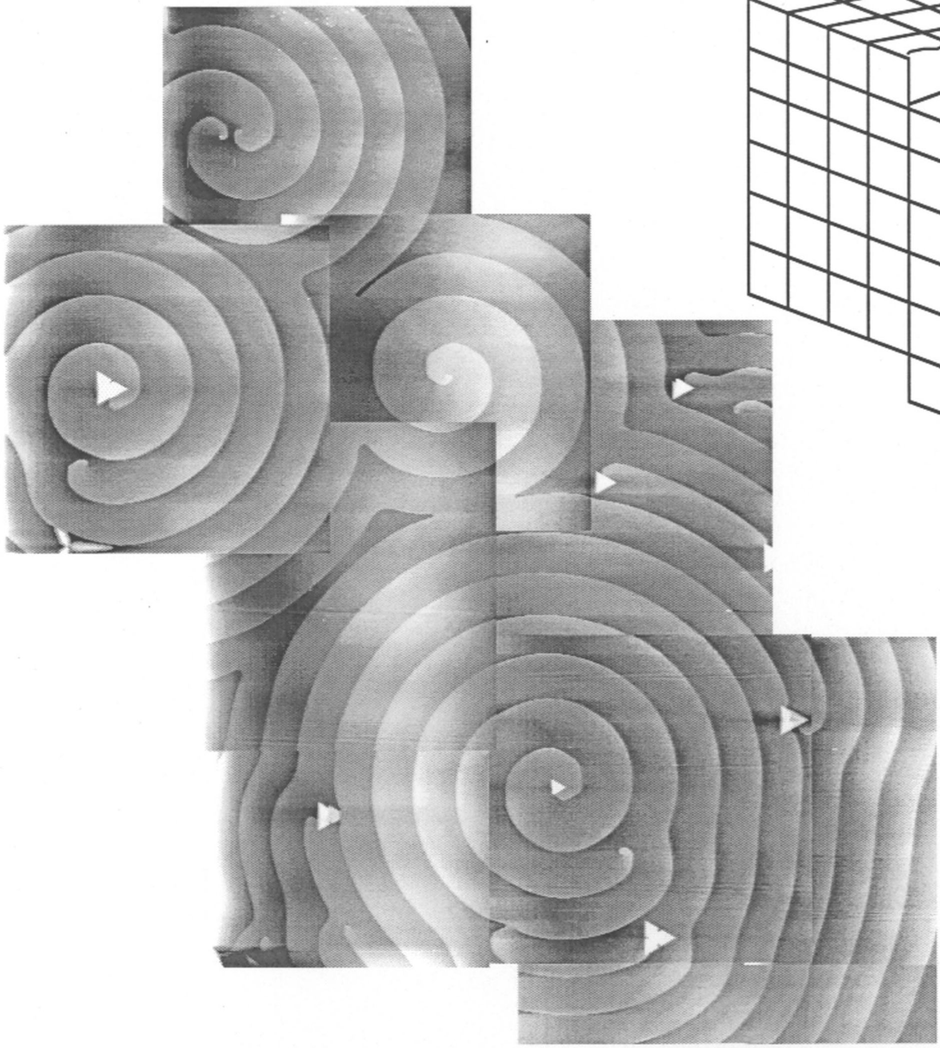
Prolate: facet moves towards the center of the crystal.

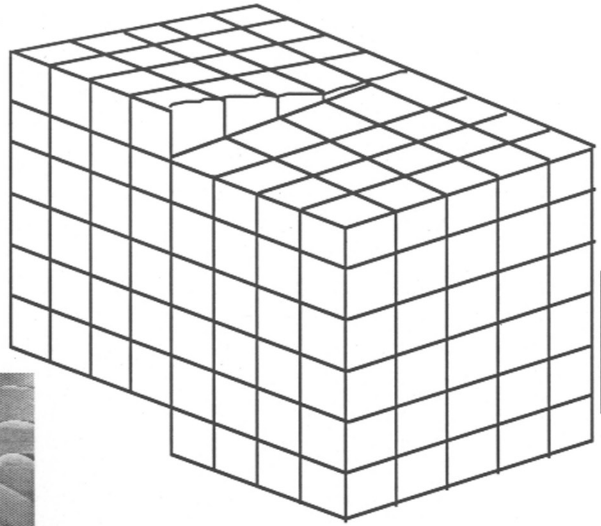
Oblate: facet moves away from the center of the crystal.

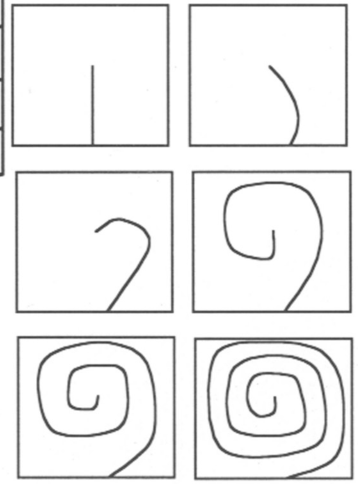
- **Assume constant volume**
- **Assume constant curvature**
- **Assume that the contact angle is preserved**

How do Real Crystals Grow?

Spiral Growth



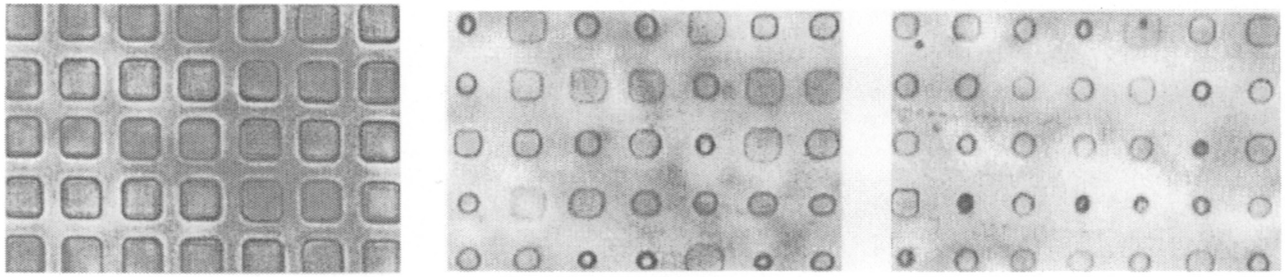




Step-producing defects allow growth without nucleation

Evidence for the Nucleation Energy Barrier and Defect Controlled Evolution

20 μm pores in Al_2O_3
oblate shapes with large $(10\bar{1}2)$ facets

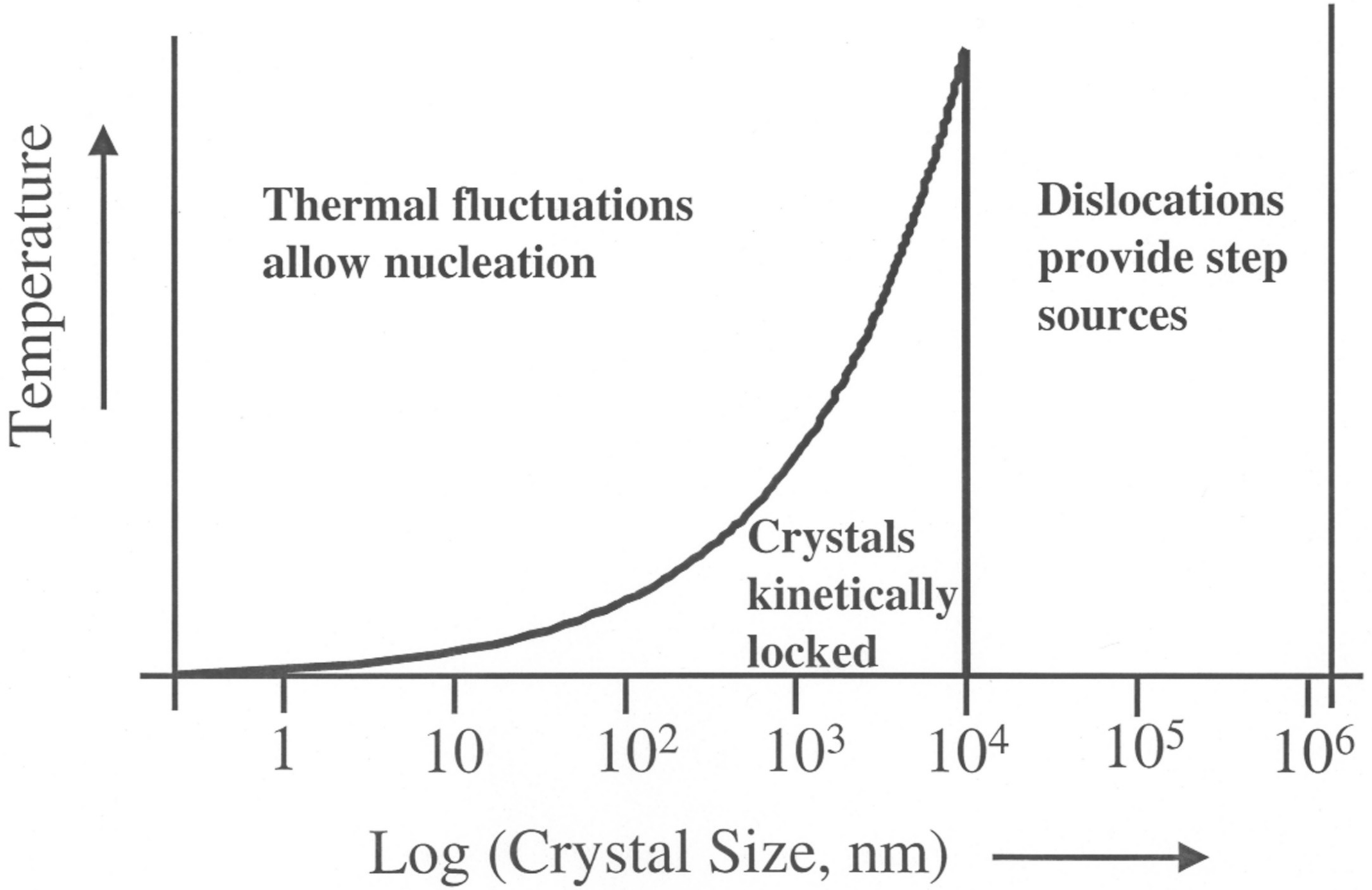


Initial **4 h at 1900 °C** **16 h at 1900 °C**

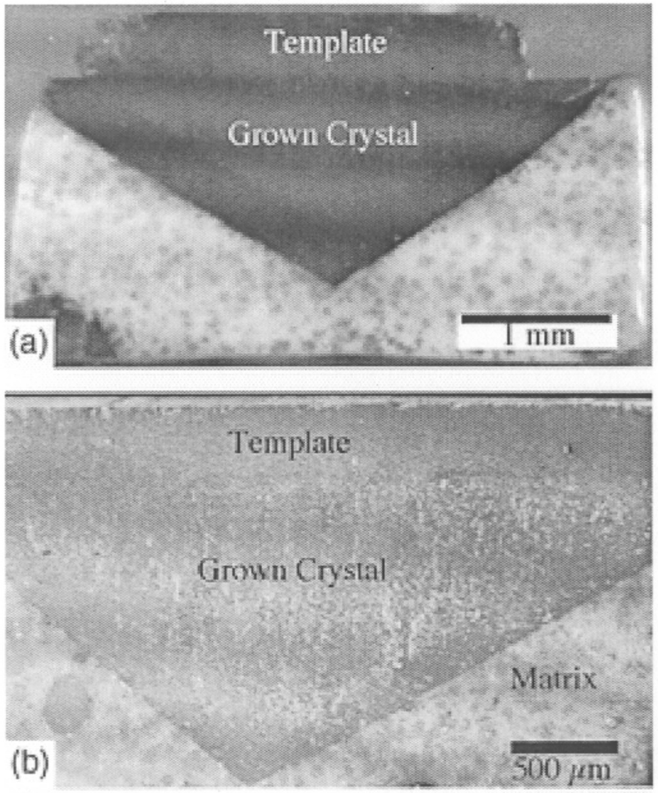
Kitayama, Narushima, Glaeser, *J. Am. Ceram. Soc.*, 83 [10] 2572-82 (2000).

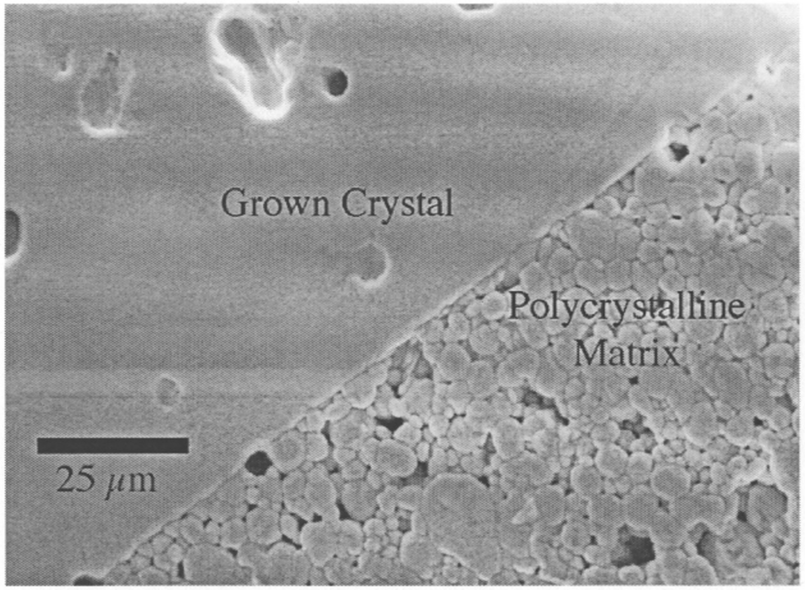
Some pores evolve to the ECS, others are stuck.

Shape Change Kinetics Depend on Size and Defect Structure (Schematic)



Size Effects are also Observed in Coarsening



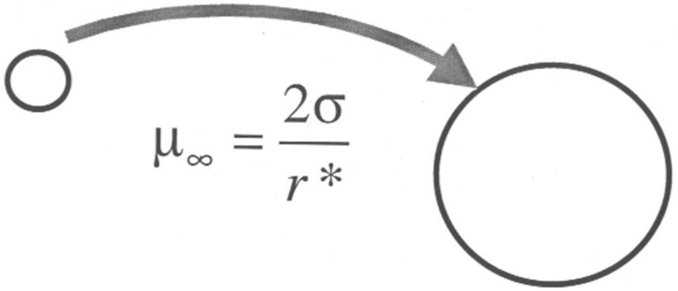


P.W. Rehrig, G.L. Messing, S. Trolier-McKinstry, "Templated Grain Growth of Barium Titanate Single Crystals," J. Am. Ceram. Soc., 83 [11] 2654–60 (2000)

- Growth occurs in a eutectic liquid
- Seed growth 790 μm/h, matrix grains ≤ 9 μm/h

Conventional Coarsening Theory

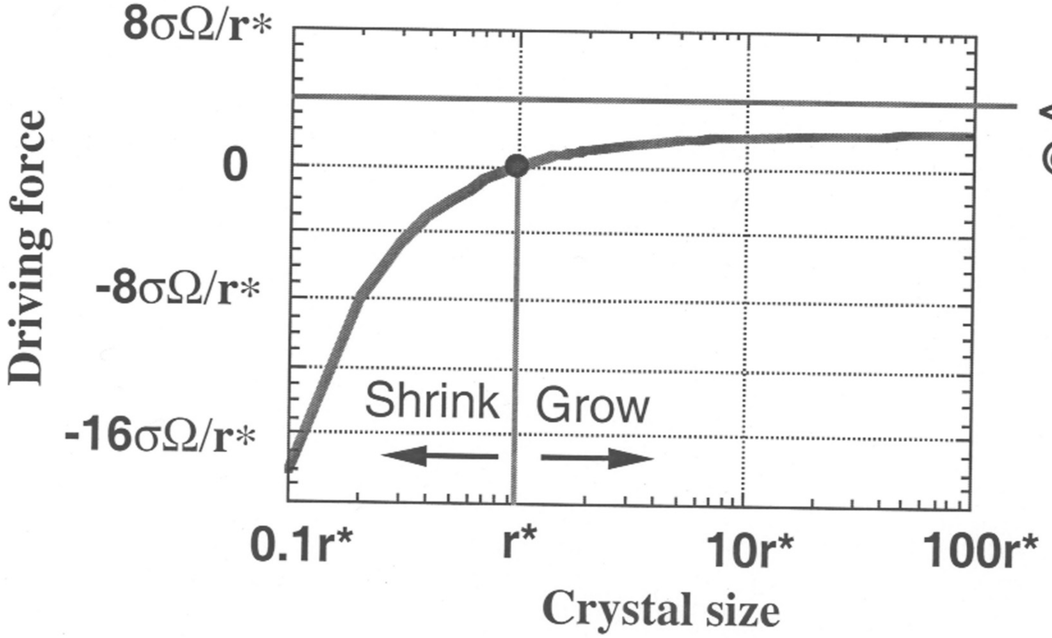
$$\mu_1 = \frac{2\sigma}{r_1}$$



$$\mu_\infty = \frac{2\sigma}{r^*}$$

$$\mu_2 = \frac{2\sigma}{r_2}$$

$$\Delta G = 2\sigma\Omega\left(\frac{1}{r^*} - \frac{1}{r}\right)$$



Assume: $r^* = 1\ \mu m$
$\sigma = 1\ J/m^2$

$2\sigma\Omega/r^* = 3 \times 10^{-23}$ J
kT @ 1500 °C = 2×10^{-20} J

- **LSW assumes growth/dissolution occurs by transport along capillarity-induced chemical potential gradients.**
- **Driving forces for growth are small compared to kT**

The Nucleation Energy Barrier

Energy barrier for crystal at r*

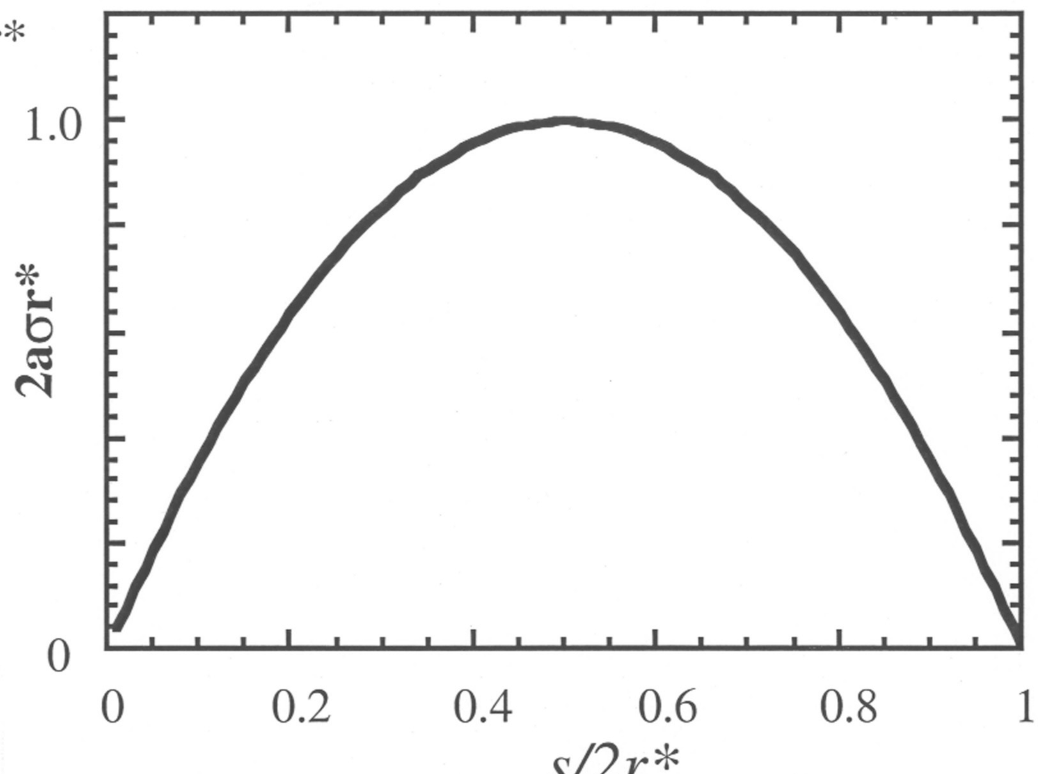
$$\varepsilon(s) = 4as\sigma - as^2 \frac{2\sigma}{r^*}$$

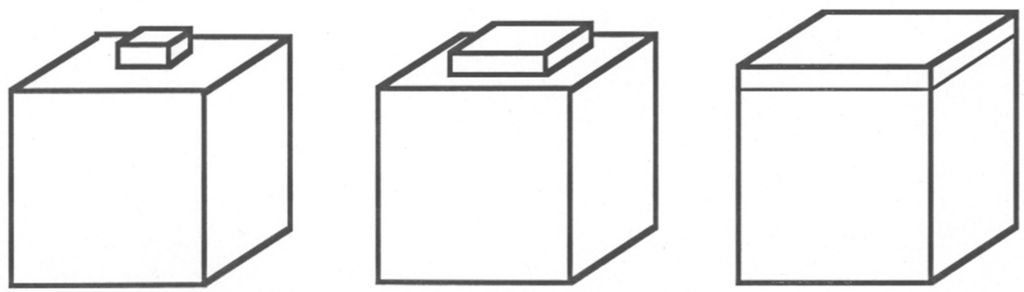
$$\varepsilon_+ = 2a\sigma r^*$$

$(L = 2\,r^*)$

$a = 2.5 \times 10^{-10}$m
$r^* = 1\times10^{-6}$m
$\sigma = 1$ J/m^2
$\varepsilon_+ = 5 \times 10^{-16}$ J >> kT

Barriers greater than 40kT are not surmounted





$s = 0.25$L $\quad$ $s = 0.5$L $\quad$ $s =$ L

NEB as a Function of Crystal Size

Layer removal

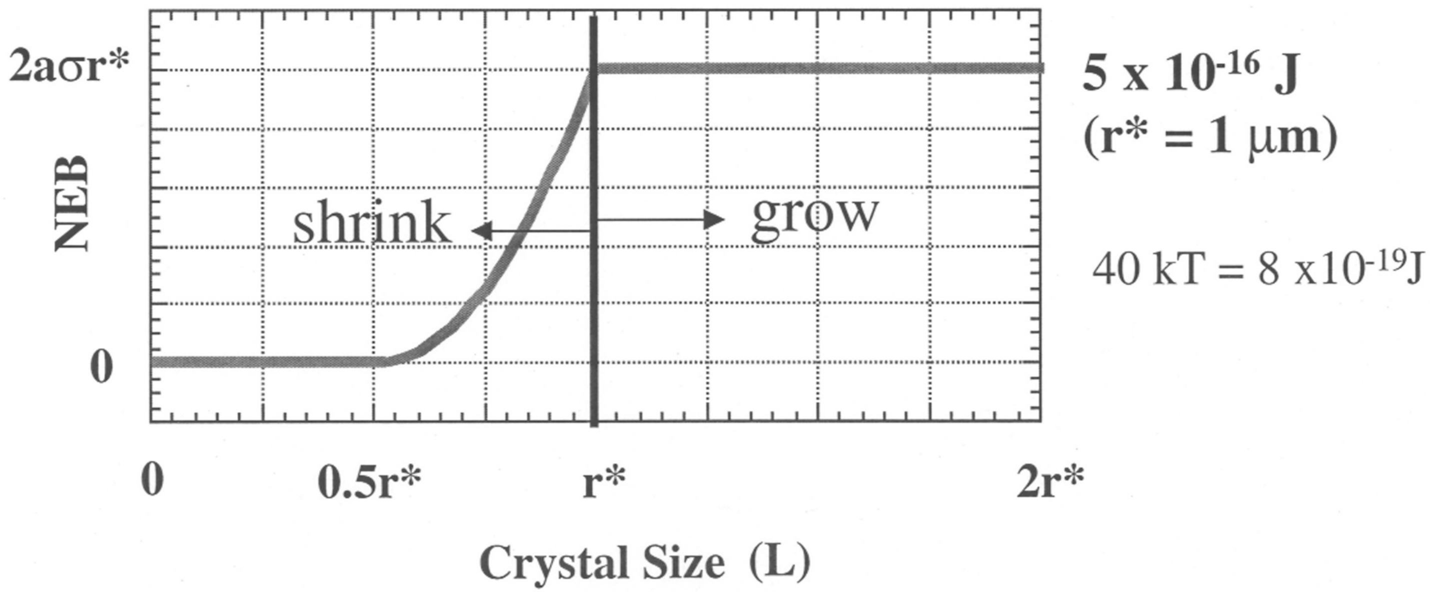
$$\varepsilon(s) = 4as\sigma - 4aL\sigma + (aL^2 - as^2)\frac{2\sigma}{r^*}$$

$$\varepsilon_- = 2a\sigma\left[R^* + L\left(\frac{L}{r^*} - 2\right)\right]$$

Layer addition

$$\varepsilon(s) = 4as\sigma - as^2\frac{2\sigma}{r^*}$$

$$\varepsilon_+ = 2a\sigma r^*$$



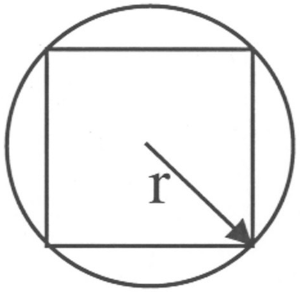
Thermal fluctuations can not support 2D nucleation during coarsening of micron-sized crystals

Model for Coarsening of Faceted Crystals

For crystals of all sizes
nucleation rate = rate material arrives at surface by diffusion

Crystal is in equilibrium with a chemical potential of

$$\mu_e = \frac{2\sigma}{r}$$



Potential selected to balance diffusion and nucleation rates

$$\mu_e < \mu_s < \mu_\infty$$

Mean field potential

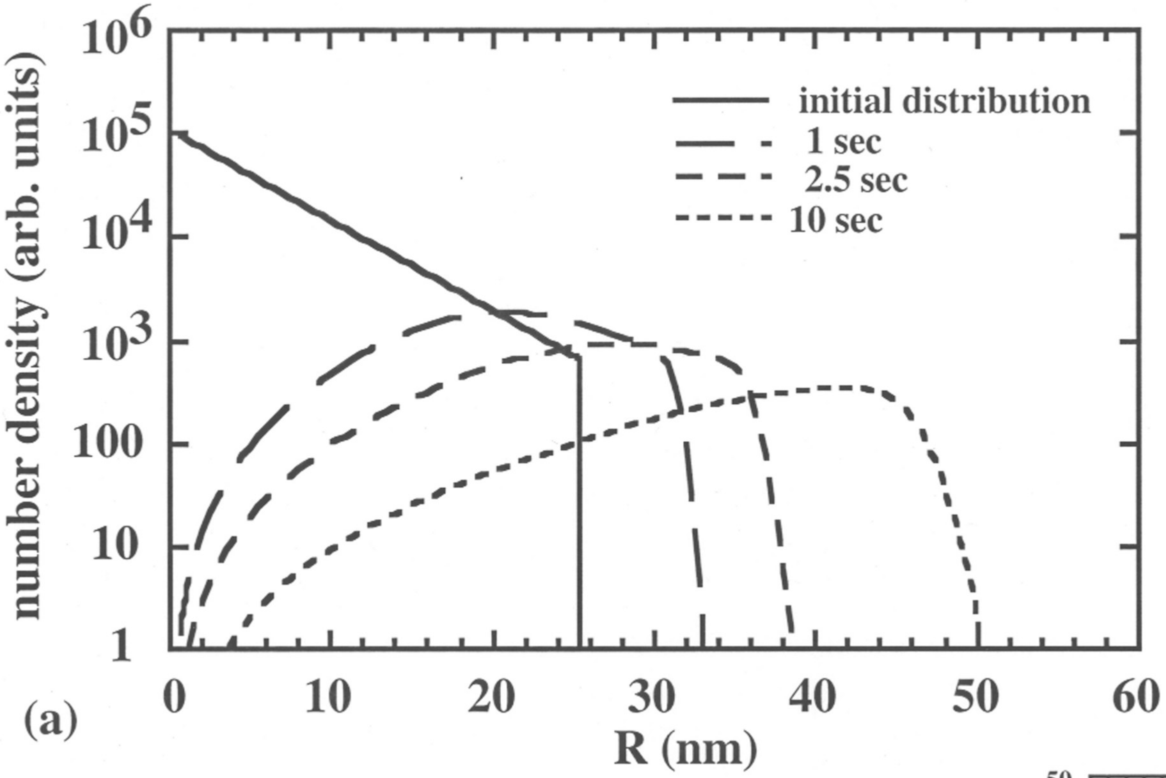
$$\mu_\infty = \frac{2\sigma}{r^*}$$

For a starting distribution, n(R), numerically determine r* and local chemical potentials (μ_s) for each crystal size class, under the constraint that the total volume is conserved.

Examine three cases:

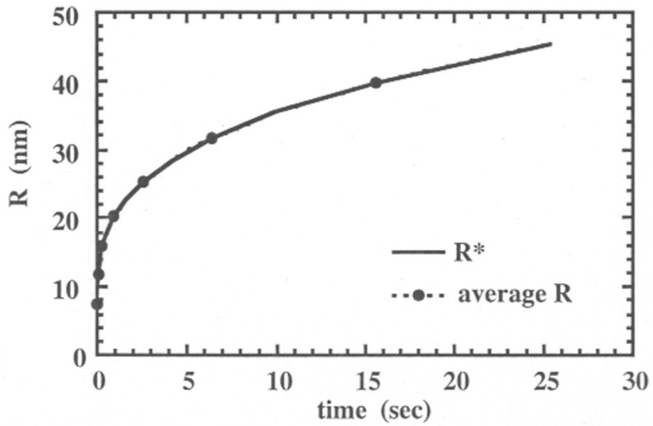
1. No crystals have a NEB; LSW
2. All crystals have a NEB
3. Most crystals have a NEB, others do not.

No Barrier to Nucleation

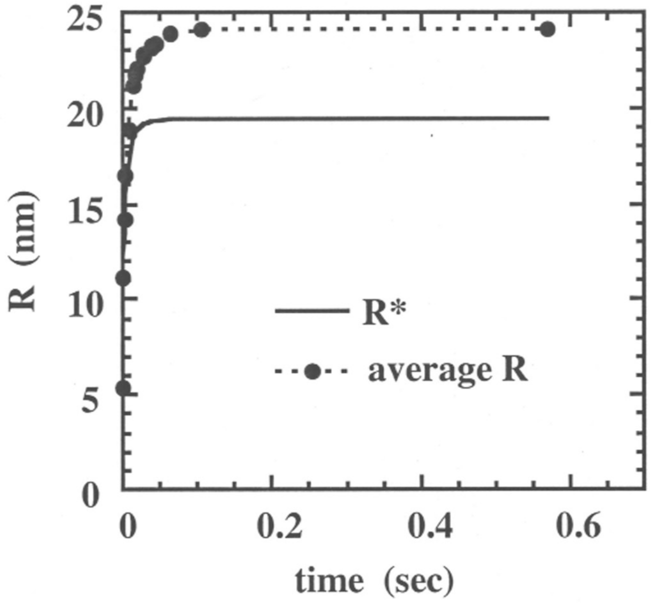


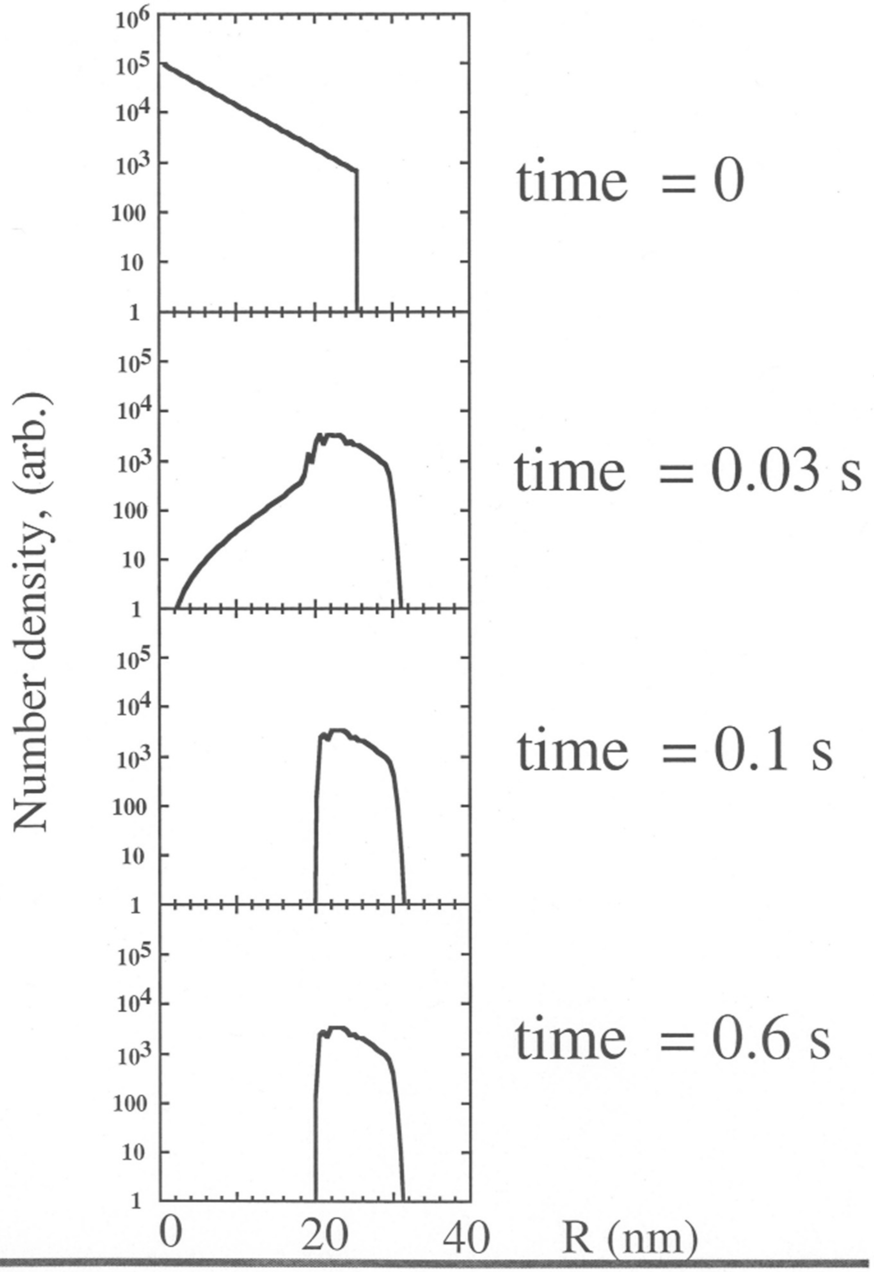
The barrier is "turned off" by lowering the surface energy to 0.001 J/m^2.

• Results are consistent with LSW theory



Coarsening with a Barrier

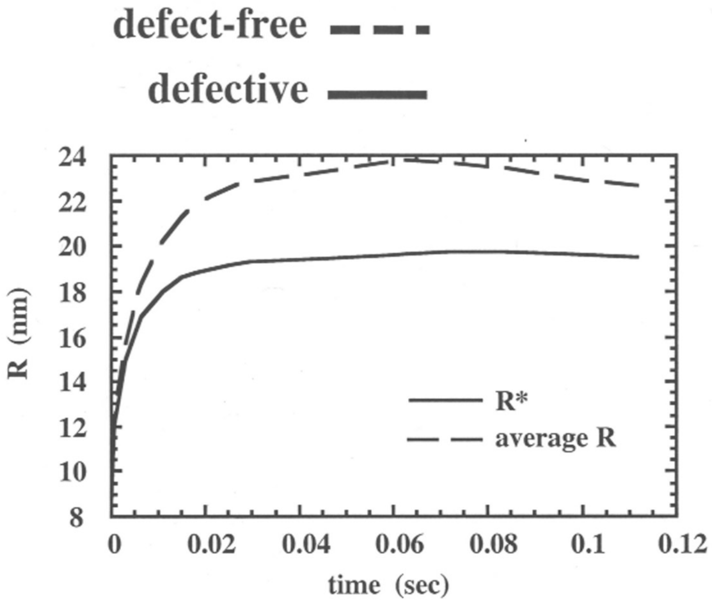




Distribution becomes frozen above a critical size where thermal fluctuations are insufficient to drive nucleation.

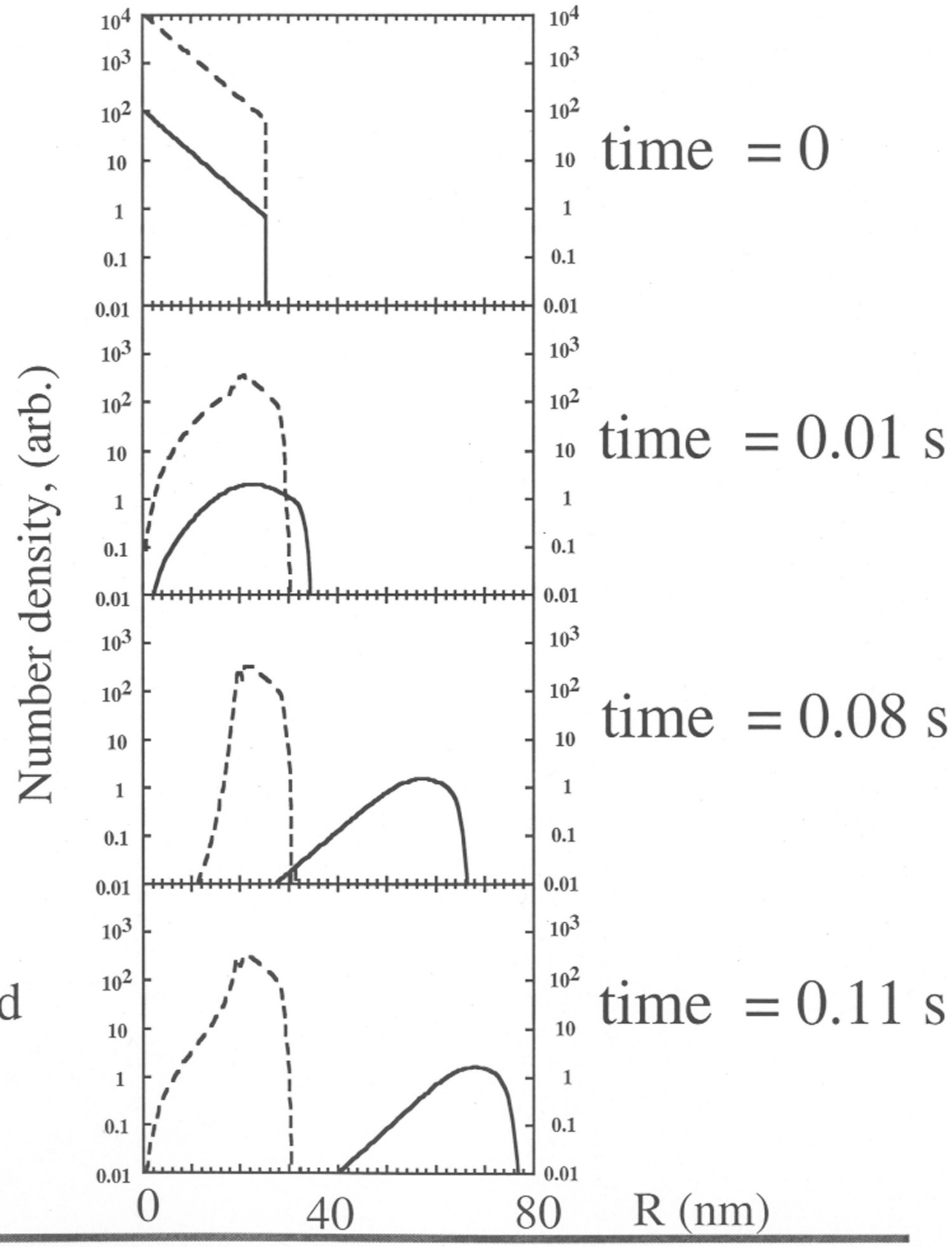
$\sigma = 0.1\ \mathrm{J/m^2}$

Ideal and Defective Crystals



• Crystals with a persistent step source grow at the expense of ideal crystals

• A bimodal distribution is developed



Predictions for Faceted Crystal Coarsening

- In populations containing a mixture of prefect and defective crystals, the crystals with step sources grow at the expense of the perfect ones.
- When the ideal crystals have been consumed, the remaining crystals no longer have an advantage, and coarsening should proceed normally.
- Large seeds, added during TGG and SSCC processing, have a higher probability of containing a defect and grow at the expense of the matrix.

Conclusions

- In systems with micron-scale crystals, capillary driving forces and thermal fluctuations are insufficient to sustain nucleation on flat surfaces; the coarsening of faceted crystals beyond this size must be defect mediated

- In populations of real crystals containing a mixture of perfect and defective particles, mass will accumulate on defective particles.

- If step producing defects are relatively rare, then abnormal coarsening will occur. If step producing defects are relatively common, then normal coarsening will occur.